

# Understanding ferromagnetism in Cr-based 3d-5d double perovskites

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(Dated: February 28, 2012)

Ferromagnetism in Cr-based double perovskites is analyzed using effective model as well as simulation approach. Starting from a microscopic model proposed recently for this class of double perovskites, an effective spin-only model is derived in the limit of large exchange coupling at the B-site. Analytic expressions for the resultant exchange coupling is derived in certain limiting cases. The behaviour of this exchange is used to provide a plausible explanation for the enhanced ferromagnetic tendency as also the enigmatic increase in Curie temperature observed in Cr-based DP-s, in the series  $\text{Sr}_2\text{CrWO}_6, \text{Sr}_2\text{CrReO}_6$  to  $\text{Sr}_2\text{CrOsO}_6$ . The superexchange between neighbouring B and B' sites is found to play a crucial role both in stabilizing ferromagnetism, especially in the latter two compounds, as well as increasing the  $T_c$ .

PACS numbers:

## I. INTRODUCTION

In recent times, ferromagnetic transition metal compounds with high  $T_c$  have come into the focus for their importance in spintronics and other technological applications. While doped rare earth manganites have been studied for decades for their CMR property, no less well known are the double perovskites, with a general formula  $\text{A}_2\text{BB}'\text{O}_6$ , A=alkaline/rare-earth metals and B/B'=transition metals. The most well known member,  $\text{Sr}_2\text{FeMoO}_6$  has a  $T_c$  of 410K, higher than most manganites<sup>1,2</sup>. Moreover, the half-metallic nature<sup>3,4</sup>, coupled with the substantial tunnelling magnetoresistance obtained in these compounds at low temperatures, especially when powdered, makes it valuable for spintronic applications<sup>5-7</sup>. The high  $T_c$  implies a strong polarization even at room temperatures, enhancing its industrial importance. In an effort to boost the  $T_c$  even further, researchers have electron doped this compound<sup>8-10,12</sup>. Although the  $T_c$  does increase in this process upto some point<sup>10,11</sup>, but it has been shown in a recent work that upon overdoping, the  $T_c$  actually decreases, and the ferromagnetism becomes unstable<sup>13,14</sup>! In fact, it gets replaced by antiferromagnetic phases. This conclusion had been derived both within model Hamiltonian approach<sup>13</sup> as well as within abinitio approach. Within the model approach, it was observed that the effective exchange interaction between Fe  $S = 5/2$  core spins changes sign as the filling increases, signalling a crossover from ferro to antiferro. Within the abinitio approach, considering the  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$  series<sup>14</sup>, it was observed that the ferromagnetic state became progressively unstable as the number of valence electrons was increased through increased doping of La, the balance tilting at an electron count of about 2.4. While the La-overdoped regime of this compound has not been investigated in detail as yet, recent experimental data support our claims regarding the disappearance of ferromagnetism on electron doping<sup>15</sup>. Hence simple electron doping by A-site cation substitution is not a very promising method for increasing  $T_c$  beyond a point. There is however, another well

known technique to change the electron filling, namely to substitute instead the B' site ion. In this case, it is well known that in Cr-based double perovskites:  $\text{Sr}_2\text{CrB}'\text{O}_6$ , as one goes across the period, substituting B' in turn as W, Re and Cr, the  $T_c$  increases progressively, reaching a high of over 700K for the Os compound. Obviously, the ferromagnetism is not becoming unstable in this series of compounds even though the filling is increasing from 1 to 2 to 3 as one goes from W to Re to Os respectively. On the contrary, it is becoming more stabilized, as signified by the increasing  $T_c$ . In this paper, we probe the role of a novel superexchange mechanism, in addition to the kinetic energy driven mechanism already prevalent, to account for this anomalous stabilization of ferromagnetic behaviour. While abinitio and variational approaches had earlier<sup>16</sup> provided a pointer to this superexchange mechanism, in this communication, we conclusively demonstrate its importance using effective exchange calculations and direct numerical simulations. The organization of the paper is as follows. In the next section, we shall briefly summarize the Hamiltonian as well as main results for the  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$  series (i.e., cation site substitution), just to serve as a reminder, and for contrast with the Cr-based series (B-site substitution). Next, we provide a brief account of the main results of abinitio studies upon these compounds, which have been reported in detail earlier. In the fourth section, we motivate a new modified Hamiltonian for this Cr-series. We proceed to derive a low-energy, spin-only model from this fermionic Hamiltonian in the next section, and analyze its magnetic properties.

## II. A-SITE CATION DOPING: BRIEF SUMMARY

A-site cation substitution can be done upon the parent compound  $\text{Sr}_2\text{FeMoO}_6$  using, for example La which has a nominal valence state of 3+, in place of Sr which has a valence state of 2+. This would correspond to electron doping of the system. Abinitio studies on this

series of compounds<sup>14</sup>, using NMTO<sup>17</sup> downfolding have shown that the relative positions of Fe and Mo  $t_{2g}$  orbitals remain almost unchanged upon La doping, only the Fermi energy shifts almost like a rigid band picture. Thereupon, total energy calculations using Vienna Abinitio Simulation Package (VASP)<sup>18</sup> showed that the magnetic ground state changed from ferro to antiferro as the electron doping increased. The spin splitting at the Fe and Mo site was also obtained by downfolding everything except the  $t_{2g}$  orbitals. It was observed that the spin-splitting at the Mo-site increased proportional to the filling, so that the Stoner  $I$  remained essentially constant. For example, in  $\text{Sr}_2\text{FeMoO}_6$  which has 1 electron per site the spin-splitting at the Mo site is about 0.13 eV, while in  $\text{La}_2\text{FeMoO}_6$ , with a filling of 3, the splitting is 0.37 eV. This showed that the moment at the Mo site is completely induced from the Cr spin, and not intrinsic. It was shown in that paper that the Hamiltonian which captures this behaviour is given by:

$$\begin{aligned}
H = & \epsilon_{Fe} \sum_{i \in B} f_{i\sigma\alpha}^\dagger f_{i\sigma\alpha} + \epsilon_{Mo} \sum_{i \in B'} m_{i\sigma\alpha}^\dagger m_{i\sigma\alpha} \\
& - t_{FM} \sum_{\langle ij \rangle > \sigma, \alpha} f_{i\sigma, \alpha}^\dagger m_{j\sigma, \alpha} - t_{MM} \sum_{\langle ij \rangle > \sigma, \alpha} m_{i\sigma, \alpha}^\dagger m_{j\sigma, \alpha} \\
& - t_{FF} \sum_{\langle ij \rangle > \sigma, \alpha} f_{i\sigma, \alpha}^\dagger f_{j\sigma, \alpha} + J_1 \sum_{i \in A} \mathbf{S}_i \cdot f_{i\alpha}^\dagger \vec{\sigma}_{\alpha\beta} f_{i\beta} \quad (1)
\end{aligned}$$

The  $f$ 's refer to the Fe sites and the  $m$ 's to the Mo sites.  $t_{FM}$ ,  $t_{MM}$ ,  $t_{FF}$  represent the nearest neighbor Fe-Mo, second nearest neighbor Mo-Mo and Fe-Fe hoppings respectively, the largest hopping being given by  $t_{FM}$ .  $\sigma$  is the spin index and  $\alpha$  is the orbital index that spans the  $t_{2g}$  manifold. The difference between the ionic levels,  $\tilde{\Delta} = \epsilon_{Fe} - \epsilon_{Mo}$ , defines the charge transfer energy. Since among the crystal-field split d levels of Fe and Mo, only the relevant  $t_{2g}$  orbitals are retained, giving rise to on-site and hopping matrices of dimension  $3 \times 3$ . The  $\mathbf{S}_i$  are 'classical' (large  $S$ ) core spins at the B site, coupled to the itinerant B electrons through a coupling  $J_1 \gg t_{FM}$ . Variants of this two-sublattice Kondo lattice model has been considered by several authors<sup>10,19-22</sup> in the context of double perovskites.

The abinitio calculations showed that the charge transfer energy  $\Delta$  remains almost fixed upon La-doping. Consequently, the doping only corresponds to increasing the Fermi energy keeping the levels fixed, thereby increasing the electron filling. If one further integrates out, or downfolds, the Mo  $t_{2g}$  degrees of freedom represented by  $m^\dagger$ , and traces over the  $f^\dagger$ -s, then one can arrive at an effective model consisting of only the Iron core spins  $\vec{S}$ , and calculate the resultant exchange interaction between them<sup>13</sup>. This exchange, when plotted at constant  $\Delta$  as a function of filling alone, exhibits a change of sign as the filling increases, as shown in Ref<sup>13</sup>. Thus, the ground state changes from ferromagnetic to antiferromagnetic at a filling of about 2.2-2.4.

### III. B' SITE SUBSTITUTION: MAIN ABINITIO RESULTS

In the series of compounds  $\text{Sr}_2\text{CrB}'\text{O}_6$ , the B' ion which is in nominal 5+ valence state corresponds to  $5d^1, 5d^2, 5d^3$  configuration of W, Re and Os respectively. These materials have been reported to have  $T_c$  as high as about 450K, 620K and 725K. with a progressive increase as one moves from  $\text{Sr}_2\text{CrWO}_6$  with one valence electron to  $\text{Sr}_2\text{CrOsO}_6$  with three valence electrons. Taking the number of valence electrons as sole consideration, the situation of  $\text{Sr}_2\text{CrWO}_6, \text{Sr}_2\text{CrReO}_6, \text{Sr}_2\text{CrOsO}_6$  is comparable to  $\text{Sr}_2\text{FeMoO}_6$ ,  $\text{SrLaFeMoO}_6$  and  $\text{La}_2\text{FeMoO}_6$ . However, unlike the Cr-B' ( $B'=\text{W, Re, Os}$ ) series, for the  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ , the ferromagnetic  $T_c$  was found to decrease with increasing La concentration (i.e., increasing number of valence electrons) and finally the antiferromagnetic phase taking over the ferromagnetic phase. The Cr-B' ( $B'=\text{W, Re, Os}$ ) series though bear two fundamental differences compared to  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$  series. Firstly, the B' ions in Cr-B' being 5d transition metals exhibit significant spin-orbit coupling which make these materials suitable for magneto-optic applications with large signal as has been discussed in Ref1. Secondly, three different chemical elements, namely W, Re and Os are involved in Cr-B' series while for  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$  series the increased electron count is achieved without any changes in the B-B' sublattice. First principle calculations using generalized gradient approximation (GGA)<sup>24</sup>, carried out using (VASP) as well as Linear Muffin Tin Orbital (LMTO) have been carried out for the total energy calculations. Thereafter, a few-band, low-energy tight binding Hamiltonian was derived using N-th order muffin-tin orbital (NMTO)<sup>17</sup> formalism. Details have been reported elsewhere<sup>16</sup>; here we recapitulate the main results.

It was observed that the moment on the B' site increased from  $0.3\mu_B$  for tungsten (W) to  $0.81\mu_B$  for Rhenium (Re) to  $1.44\mu_B$  for Osmium. The total moment, on the other hand, goes from  $2\mu_B$  in W to  $1\mu_B$  in Re to  $0\mu_B$  in Os. It is observed that although the total moment decreases in steps commensurate with the filling, and the Cr moment remains almost fixed, the moment at the B' site increases drastically, pointing to the growing localization of electrons on this site.

To probe this issue in more detail, the Sr, Oxygen orbitals as well as the  $e_g$  orbitals of Cr and B' ions were downfolded using NMTO formalism, keeping only the Cr and B'  $t_{2g}$  orbitals. It was observed that the spin splitting at the B' site increased from 0.06 eV at the W site to 0.31 at the Re site to 0.53 at the Os site. This is obviously a much faster increase than the filling would dictate, indicating that the Stoner  $I$  is itself increasing. If we multiply the splitting for W, i.e., 0.06 by 2 and 3 respectively, then the extra amount must correspond to a different energy scale in the problem. Let us call this energy scale as  $J_2$ , while the traditional extremely large spin splitting at the B site, or Chromium site defines the

other exchange energy scale,  $J_1$ .

Another important point which emerges out of abinitio calculations is the progressive increase in the charge transfer energy  $\Delta$  as one goes across the series from W to Re to Os. It increases from 0.51 eV in W, to 0.9 in Re, to 1.35 in Os. This situation is to be contrasted with the nearly constant  $\Delta$  in the  $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$  series. Thus, it may be summarized that both  $\Delta$  and  $J_2$  are increasing in the Cr-series from W to Re to Os compounds, although  $J_2$  is usually much less than  $\Delta$ .

#### IV. HAMILTONIAN

From the above considerations, it is obvious that there exists a different exchange energy scale to the problem, apart from the spin splitting at the Cr site  $J_1$ , which, being related to the Hund coupling, for all practical purposes can be considered infinite. The increasing localized character of the moment on the  $B'$  site makes superexchange an obvious candidate for this new energy scale. Hence we have added a superexchange term to the Hamiltonian corresponding to superexchange between the  $t_{2g}$  spin on the  $B$  site, and the electron spin on the  $B'$  site. Hence, the representative Hamiltonian is given by:

$$\begin{aligned}
H = & \epsilon_{Fe} \sum_{i \in B} f_{i\sigma\alpha}^\dagger f_{i\sigma\alpha} + \epsilon_{Mo} \sum_{i \in B'} m_{i\sigma\alpha}^\dagger m_{i\sigma\alpha} \\
& - t_{CB/} \sum_{\langle ij \rangle \sigma, \alpha} f_{i\sigma, \alpha}^\dagger m_{j\sigma, \alpha} - t_{B'B/} \sum_{\langle ij \rangle \sigma, \alpha} m_{i\sigma, \alpha}^\dagger f_{j\sigma, \alpha} \\
& - t_{CC} \sum_{\langle ij \rangle \sigma, \alpha} f_{i\sigma, \alpha}^\dagger f_{j\sigma, \alpha} + J_1 \sum_{i \in A} \mathbf{S}_i \cdot f_{i\alpha}^\dagger \vec{\tau}_{\alpha\beta} f_{i\beta} \\
& + J_2 \sum_{i \in B} \mathbf{S}_i \cdot m_{i\alpha}^\dagger \vec{\sigma}_{\alpha\beta} m_{i\beta} \quad (2)
\end{aligned}$$

This spin-fermion Hamiltonian is in general difficult to solve exactly, but some headway in the direction of understanding the low-energy magnetic behaviour can be made if one can obtain a spin-only model from this with an effective exchange. In principle this should be possible by tracing out the fermion degrees of freedom, but that is a herculean task considering the multitude of possible configurations. Instead, we consider the approximate but enlightening procedure of Self-Consistent Renormalization (SCR) devised by Kumar and Majumdar<sup>23</sup>.

#### V. DERIVATION OF EFFECTIVE SPIN MODEL

In an earlier paper<sup>13</sup>, I had obtained an effective spin model from the two-sublattice Kondo lattice model (Eqn 1) appropriate for the Fe-series

( $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ ) using the procedure of SCR. In the action corresponding to this Hamiltonian, all but the last term is translationally invariant, hence can be Fourier transformed and written in terms of the bare Green's function. Thereafter, the Molybdenum degrees of freedom can be integrated out, and the Iron degrees of freedom traced over, after taking the limit of  $J_1 \rightarrow \infty$ , to obtain an effective model containing only the Iron spins. One may imagine that the same procedure may be followed in this case. There is a fundamental difficulty in this case though, due to the fact that there is spin-disorder even on the Molybdenum site, making it impossible to diagonalize and integrate out the Molybdenum degrees of freedom. Hence, the entire procedure of thinning of degrees of freedom has to be done in real space. The action corresponding to the Hamiltonian in Eqn 2 is given by:

$$\begin{aligned}
\mathcal{A} = & \sum_{i\omega_n} \left[ (i\omega_n - \epsilon_{Fe}) \sum_{i\sigma} f_{i,n,\sigma}^\dagger f_{i,n,\sigma} + (i\omega_n - \epsilon_{Mo}) \sum_{i\sigma} m_{i,n,\sigma}^\dagger m_{i,n,\sigma} \right. \\
& \left. + t_{FM} \sum_{\langle ij \rangle} (f_{i,n,\sigma}^\dagger m_{j,n,\sigma} + h.c.) \right. \\
& \left. + J_1 \sum_{i\alpha\beta} \vec{S}_i \cdot f_{i,n,\sigma}^\dagger \vec{\tau}_{\alpha\beta} f_{i,n,\beta} + J_2 \sum_i \vec{S}_i \cdot m_{i,n,\sigma}^\dagger \vec{\sigma}_{\alpha\beta} m_{i,n,\beta} \right] \quad (3)
\end{aligned}$$

Now, since the spin orbit coupling at the  $B'$  site is large for the 5d elements like Re and Os compared to the 4d elements like Mo, the onsite spin anisotropy is also expected to be high. Let us choose our axis of quantization along this anisotropy axis, whereupon we need only consider the diagonal components of the last  $J_2$  term. Hence, the action can be written as:

$$\begin{aligned}
\mathcal{A} = & \sum_{i\omega_n} \left[ (i\omega_n - \epsilon_{Fe}) \sum_{i\sigma} f_{i,n,\sigma}^\dagger f_{i,n,\sigma} + t_{FM} \sum_{\langle ij \rangle} (f_{i,n,\sigma}^\dagger m_{j,n,\sigma} + h.c.) \right. \\
& \left. + J_1 \sum_{i\alpha\beta} \vec{S}_i \cdot f_{i,n,\alpha}^\dagger \vec{\tau}_{\alpha\beta} f_{i,n,\beta} + \sum_{i,\alpha,\beta,\delta} m_{i,n,\alpha}^\dagger M_{\alpha\beta} m_{i,n,\beta} \right] \quad (4)
\end{aligned}$$

where the matrix  $M$  is given by:  $M = (i\omega_n - \epsilon_{Mo})\mathbf{I} + J_2 S_{i+\delta}^z \sigma_z$ . Hence, first taking the  $J_1 \rightarrow \infty$  limit<sup>22</sup>, and then integrating the  $B'$  degrees of freedom out, we get the following form for the action:

$$\begin{aligned}
\mathcal{A} = & \sum_{i,n} (i\omega_n - \epsilon_{Fe}) \gamma_{i,n}^\dagger \gamma_{i,n} \\
& - \sum_{\langle \langle ij \rangle \rangle} \frac{t_{FM}^2}{i\omega_n - \epsilon_{Mo} + J_2 \sum_\delta S_\delta^z} \cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} \gamma_{i,n}^\dagger \gamma_{j,n}
\end{aligned}$$

$$- \sum_{\langle\langle i,j \rangle\rangle} \frac{t_{FM}^2}{i\omega_n - \epsilon_{Mo} - J_2 \sum_{\delta} S_{\delta}^z} \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} \gamma_{i,n}^{\dagger} \gamma_{j,n} \quad (5)$$

where  $\gamma_{i,n}$  refer to transformed spinless Fermion operators at the Iron site, while  $\theta_i$  refer to the azimuthal angle made by the Fe core spins with the z-axis. Following usual practice, we have neglected the Berry's phase degrees of freedom connected with the polar angles.

Hence, if we consider total energy  $U = -\left\langle \frac{\partial A}{\partial \beta} \right\rangle$  as before<sup>13</sup>, then we get:

$$U = \sum_{\langle\langle ij \rangle\rangle} t_{FM}^2 \left[ \frac{(2i\omega_n - \Delta + J_2 \sum_{\delta} S_{\delta}^z)}{(i\omega_n - \Delta + J_2 \sum_{\delta} S_{\delta}^z)^2} \cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} + \frac{(2i\omega_n - \Delta - J_2 \sum_{\delta} S_{\delta}^z)}{(i\omega_n - \Delta - J_2 \sum_{\delta} S_{\delta}^z)^2} \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} \right] G_{n,ij} \quad (6)$$

So far, no approximation has been made except that  $J_2 \ll J_1$  and a large anisotropy at the  $B'$  site. However, to actually calculate the exchange from this expression, one first needs to start with some spin background, say random, and calculate the Iron Green's function in real space in this background using the original Hamiltonian 2. Then, one needs to recalculate the spin background from the effective spin Hamiltonian 6 again using some technique like Monte Carlo. This procedure, to be repeated till self-consistency, defines the technique of Self-consistent Renormalization<sup>23</sup>. The entire procedure is however numerically expensive and difficult. We shall, in the next section, instead, try to calculate the exchange analytically in certain simple arrangement of the background spins: namely fully ordered ferromagnetic configuration. This can act as the first step of the SCR procedure, which will be taken up in a future work. As we shall see, it will give us an important analytic pointer at the actual magnetic ground states possible in these compounds.

## VI. EXCHANGE IN ORDERED SPIN BACKGROUND

It is to be noticed that unlike our previous SCR formulation<sup>13</sup> the action no longer has full spin-rotational invariance, owing to the anisotropy. (Notice that putting  $J_2 = 0$  recovers the familiar rotationally invariant Anderson-Hasegawa form.) Hence, even if we start with a perfectly ordered spin background with all spins parallel, we must also choose an orientation relative to the anisotropy axis. We consider 3 cases. In the following, we replace  $\epsilon_{Fe} = 0$ , and  $\epsilon_{Mo} = \Delta$  for convenience. Henceforth,  $J_2$  will mean  $zJ_2$ , where  $z$  is the coordination number.

First, we consider the case  $\theta_i = 0$  for all sites. Then, translational invariance is restored, and we can write the relevant terms of the action 5 in momentum space and

calculate the exchange as follows:

$$\mathcal{A} = \sum_{k,n} \left( i\omega_n - \frac{t_{FM}^2}{i\omega_n - \Delta - J_2} \right) \gamma_{kn}^{\dagger} \gamma_{kn} \quad (7)$$

Now we calculate  $U = -\left\langle \frac{\partial A}{\partial \beta} \right\rangle$ , to obtain

$$U = \sum_{kn} \frac{t_{FM}^2 (2i\omega_n - \Delta - J_2)}{(i\omega_n - \Delta - J_2)^2} G_{kn} \quad (8)$$

Evaluating the Matsubara sum,

$$J_{ij}^{eff} = \sum_k \frac{1}{2} [E_{k+} n_F(E_{k+}) + E_{k-} n_F(E_{k-}) - (\Delta + J_2) n_F(\Delta + J_2)] e^{\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \quad (9)$$

where  $E_{k\pm} = \frac{\Delta + J_2 \pm \sqrt{(\Delta + J_2)^2 + 4\epsilon_k^2}}{2}$ . This gives the final expression for the exchange which has to be evaluated on a square lattice.

The case of  $\theta_i = \pi$  gives, proceeding in a similar fashion,

$$J_{ij}^{eff} = \sum_{k,} [E_{k+} n_F(E_{k+}) + E_{k-} n_F(E_{k-}) - (\Delta + J_2) n_F(\Delta + J_2)] e^{\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \quad (10)$$

The same as  $\theta = 0$ ! This is not surprising, since uniaxial anisotropy does not distinguish between  $\theta = 0$  and  $\theta = \pi$ . Now, let us consider the case of  $\theta_i = \frac{\pi}{2}$ .

$$\mathcal{A} = \sum_{kn} \left[ i\omega_n - \frac{1}{2} \frac{t_{FM}^2}{i\omega_n - \Delta} - \frac{1}{2} \frac{t_{FM}^2}{i\omega_n - \Delta} \right] \gamma_{kn}^{\dagger} \gamma_{kn} \quad (11)$$

Hence,

$$U = \sum_{kn} \frac{1}{2} \left[ \frac{\epsilon_k^2 (2i\omega_n - \Delta)}{(i\omega_n - \Delta)^2} + \frac{\epsilon_k^2 (2i\omega_n - \Delta)}{(i\omega_n - \Delta)^2} \right] \langle \gamma_{kn}^{\dagger} \gamma_{kn} \rangle \quad (12)$$

Thus  $J_2$  drops out entirely! Thus, the expression for the exchange here would coincide with that for  $J_2 = 0$  evaluated earlier<sup>13</sup>, which is also not surprising because the anisotropy axis has no component along the perpendicular direction, so that the superexchange has no effect on spin configurations along this direction. Replacing the Green's function,

$$U = \sum_{kn} \left[ \frac{(2i\omega_n - \Delta)}{(i\omega_n - \Delta)^2} \right] \times \left( \frac{\epsilon_k^2}{i\omega_n - \frac{\epsilon_k^2}{(i\omega_n - \Delta)}} \right) \quad (13)$$

$$(14)$$

This upon evaluation of the Matsubara sum gives the familiar expression<sup>13</sup>  $U = \sum_k [E_{k+} n_F(E_{k+}) + E_{k-} n_F(E_{k-}) - \Delta n_F(\Delta)]$  as before. This is to be expected, since the anisotropy, and consequently, the superexchange, will have no effect in a

direction perpendicular to the easy axis.

Finally we write the exchange for a general  $\theta_i = \theta$ .

$$J_{ij} = t_{FM}^2 \sum_{kn} e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} \left[ \frac{\cos^2 \frac{\theta}{2} (2i\omega_n - \Delta - J_2 \cos \theta)}{(i\omega_n - \Delta - J_2 \cos \theta)^2} + \frac{\sin^2 \frac{\theta}{2} (2i\omega_n - \Delta + J_2 \cos \theta)}{(i\omega_n - \Delta + J_2 \cos \theta)^2} \right] \times G_{kn} \quad (15)$$

where

$$G_{kn}^{-1} = i\omega_n - \frac{\epsilon_k^2 [(i\omega_n - \Delta) + J_2 \cos^2 \theta]}{(i\omega_n - \Delta)^2 - J_2^2 \cos^2 \theta} \quad (16)$$

## VII. RESULTS

The results of the exchange calculations are shown here. For the case of  $\theta = 0$  (up) the exchange is as shown in Fig 1. Since we are only interested in looking at the ferromagnetic phase, hence only the dominant nearest neighbour exchanges are shown. As explained earlier, the same graph is obtained for the  $\theta = \pi$  (down) case. For comparison, the  $J = 0$  curve for the same  $\Delta$  is also shown<sup>13</sup>. This may also be thought to be the exchange data for the  $\theta = \pi/2$  case. Two effects are immediately observed. Firstly, the extent of the ferromagnetic phase in the filling regime increases for the finite superexchange case, as compared to no superexchange. This is probably why for an extended filling regime, the ferromagnetic behaviour persists rather than the antiferromagnetic behaviour, in the 3d-5d compounds. In particular, while the exchange already becomes positive for a filling of  $n \approx 0.7$  for the  $J_2 = 0$  case, it continues to be positive way beyond  $n = 1$  for finite  $J_2$ . Secondly, the magnitude of the negative part is also larger, proving that the ferromagnetic  $T_c$  is enhanced by superexchange. Another interesting point to note is that the exchange continues to be large and negative till about  $n = 1$ , which corresponds to  $N = 3$  in the real double perovskites owing to  $t_{2g}$  degeneracy (eg.  $\text{Sr}_2\text{CrOsO}_6$ ), while its magnitude diminishes beyond that. The point  $n = 2$  shows a strong isolated antiferromagnetic tendency, possibly due to the filling of the Mo level with opposite spin in the half-metallic state.

Next, to bring these results in perspective, and establish them on a sound footing, we also performed extensive numerical simulations of the original spin-Fermion model Hamiltonian, using the technique of exact diagonalization coupled with Monte Carlo (ED+MC). Calculations performed in real space on a  $8 \times 8$  cluster is shown in the figure Fig 2. We used  $\Delta = -2$  and  $J_2 = 1$  as before. It is found that inclusion of the  $J_2$  term in the Hamil-

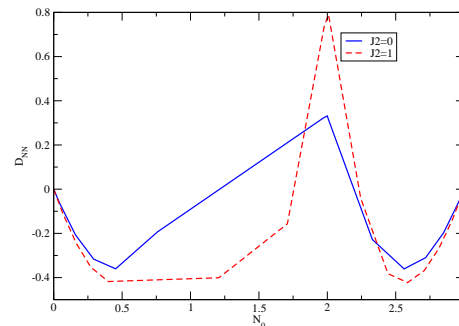


Figure 1: Exchange vs filling obtained from SCR, compared between cases with and without superexchange

tonian not only results in a tremendous increase in the Curie temperatures, but also in the proliferation of the ferromagnetic phase to higher fillings. In fact, for these regime of parameters, the ferromagnetic phase is found to make substantial entries into those regions of filling which were earlier reserved for the antiferromagnetic phases<sup>13</sup>. However, both effects are far more augmented than suggested by the SCR calculations. Of course, the SCR is performed assuming ordered spin backgrounds appropriate at low temperatures and also only one loop of the actual SCR process is performed to derive the analytical expressions given in this paper, hence it should only be considered as a pointer to the actual renormalization effects close to  $T_c$ . Interestingly, in the exact numerical simulations, both the ferromagnetic lobes at low and high filling join together in the case of finite  $J_2$ , giving a maximum  $T_c$  at  $N=1$  (which corresponds to  $N=3$  considering the  $t_{2g}$  degeneracy in the real material). This is consistent with the enigmatic high  $T_c$  observed in the compound  $\text{Sr}_2\text{CrOsO}_6$ <sup>25,27</sup>. Also, it substantiates the view that this compound is at the threshold of a magnetic and electronic transition<sup>25</sup>. Thus the mechanism of superexchange coupling between B and B' sites provides an alternate, and more acceptable mechanism for the  $T_c$  increase, rather than the Hubbard U mechanism invoked earlier<sup>21</sup>.

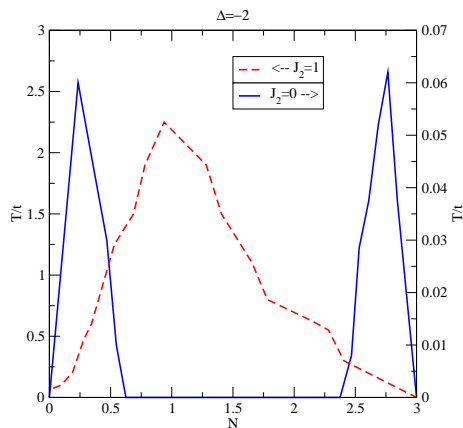


Figure 2:  $T_c$  vs  $N$  ferromagnetic part of phase diagram from  $8 \times 8$  cluster compared between  $J_2=0$  and  $J_2=1$  ( $\Delta = -2$ )

### VIII. SUMMARY AND OUTLOOK

Using the combination of effective exchange calculations within SCR and direct numerical simulations of the

microscopic Hamiltonian, we showed that the superexchange is the main player in enhancing  $T_c$  as well as stabilizing ferromagnetism in the Cr-compounds. Spin-orbit coupling breaks the rotational symmetry on the B' site, so that different orientations of spin configurations have to be considered for the SCR. Amongst the configurations considered, those along the easy axis are found to increase the effective nearest neighbour ferromagnetic exchange, as well as contribute to the increase in the filling extent of the ferromagnetic phase. Both are signatures of stabilization of the ferromagnetic phase, which results in the increase in  $T_c$ , and continuation of the ferro phase to higher fillings, as for Rh and Os compounds. Extensive numerical simulations are found to reproduce both of this behaviour, and provides a sound backing to the proposed model Hamiltonian as an useful one for describing the behaviour of Cr-based 3d-5d double perovskites.

### IX. ACKNOWLEDGMENT

The author gratefully acknowledges discussions with M. Randheria, D. D. Sarma, P. Majumdar and T. Saha Dasgupta.

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  - <sup>26</sup> In real double perovskites, due to the threefold  $t_{2g}$  degeneracy, there are a total of nine degrees of freedom per Fe-Mo pair, consisting of three at Fe site and six at Mo site. Hence, to compare with experiments, our x-axes should be

multiplied by 3.

- <sup>27</sup> We have deliberately considered a larger value of  $J_2$  than usually found in real Cr-based DP-s to underline the strong  $T_c$  enhancement and ferromagnet-proliferation effects. Ac-

tual values of  $J_2$  may leave an window for the antiferromagnetic phases as well. The effects of phase competition in this Hamiltonian will be considered in a later work.